

A MODEL FOR THE ISOTHERMAL PLASTOMETRIC BEHAVIOR OF COALS

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Introduction

The plasticity of bituminous coals in the range 350–500°C is of critical importance in thermomechanical fluidization such as is required for coal pumping by heated screws (1–3) and in hydrogenolysis in the absence of added solvent (4,5). The fact that the optimum reaction temperatures for three major current liquefaction technologies are nearly identical (6) and are close to the fluidity maxima for many plastic coals suggests that the processes comprising coal "melting" are critically important to hydroliquefaction. More generally, coal plasticity is obviously involved in caking problems (7–10).

The most widely used method of measuring coal plasticity was developed by Gieseler (11). With minor modifications this remains a standard procedure (12); its relationship to other measurements has been discussed elsewhere (13). This method measures the resistance of a mass of well-packed pulverized coal to the rotation of a rabble-arm stirrer which is driven through a constant-torque clutch. At low temperatures the solid mass completely immobilizes the stirrer shaft. In the standard Gieseler procedure the coal is heated at a uniform rate of 3°C/min. As the coal begins to soften -- typically at about 390°C -- the stirrer shaft commences to turn slowly. As temperature increases the coal becomes more fluid and the shaft turns more rapidly, eventually achieving a maximum rate. The coal melt -- actually a heterogeneous mixture of solids, molten phase and gaseous pyrolyzate -- then undergoes a thickening or "coking"; the stirrer shaft turns progressively more slowly, and eventually stops. Gieseler data are recorded in units of dial divisions per min (ddpm), where 100 ddpm = 1 shaft rotation per min. For three bituminous coals of varying plasticity the standard Gieseler data are shown in Table 1.

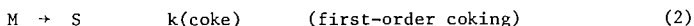
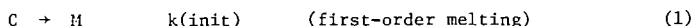
The Isothermal Model

It is often useful to study phenomena under isothermal conditions. Gieseler plastometry lends itself to such studies, since sample warmup time in the standard crucible (2–3 min.) is short in comparison with the usual melting/coking time scale (20–120 min.). Isothermal Gieseler plastometry has been explored by Fitzgerald (14,15) and by Van Krevelen and coworkers (16,17). A plot of $\log(\text{ddpm})$ against time shows a long linear coking region (14,15).

Figure 1 (open circles) shows the isothermal plastometric curves at 410–2°C obtained with the three coals described in Table 1. Both the maximum fluidities

and the periods of fluidity are seen to vary substantially among these coals.

The linearity of the coking slopes has been interpreted to imply a sequence of first-order reactions (14-17):

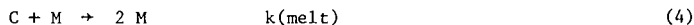


where C, M and S represent the meltable portion of the original coal, the fraction which is molten (metaplast), and the fraction which is resolidified (coked). This scheme gives rise to the rate law:

$$d[M]/dt = k_i[C] - k_c[M] \quad (3)$$

There are two problems with this scheme. First, it does not generate model curves which resemble observed curves. Specifically, it predicts the rate of increase of fluidity during the softening process to decelerate progressively, while in fact this increase is exponential with time over most of the melting period. Second, this scheme specifically assumes that Gieseler fluidity is a linear measure of the molten fraction or metaplast; but that assumption is mistaken, as we will show.

For the purpose of more closely modeling the actual isothermal curves we propose a second melting process, such that the rate of increase of fluidity is dependent upon the concentrations of both metaplast and unmelted fraction:



The rate law now acquires a third term:

$$dF/dt = k_i[C] + k_m[C][M] - k_c[M] \quad (5)$$

(We use F for fluidity, rather than [M] for metaplast, on the left-hand side). The virtue of Equation 5 is that, for most isothermal runs, it can provide a fairly good fit to the experimental data, and therefore can define the experimental curves in terms of numerical constants associated with the melting and coking processes. The solid points in Figure 1 are values generated by the Equation 5 model, using the values given in Table 2. It is a characteristic of this model that the experimental points in the vicinity of maximum fluidity tend to be higher than those generated by the model. This may reflect formation of gas bubbles, which lead to anomalously high experimental readings.

In applying this model, the least-squares melting and coking slopes are calculated from the experimental data; we use all data between 1 ddpm and one fourth the maximum observed fluidity. The extrapolated maximum fluidity (emf) and the time of maximum fluidity are taken from the intersection of these slopes.

From these determinations, approximate values for the model constants can be estimated empirically from the cubic equations:

$$\frac{m(\text{melt})}{k(\text{melt})} = -0.3179 + .71507 \times R - .15991 \times R^2 + .012348 \times R^3 \quad (6)$$

$$\frac{m(\text{coke})}{k(\text{coke})} = -0.6934 + 1.1504 \times R - .26779 \times R^2 + .020826 \times R^3 \quad (7)$$

$$\ln[k(\text{init})] = -16.127 + 2.8478 \times P - .25098 \times P^2 + .005726 \times P^3 \quad (8)$$

where $m(\text{melt})$ and $m(\text{coke})$ denote the melting and coking slopes, $R = m(\text{melt})/m(\text{coke})$, and $P = [(m(\text{melt}) + m(\text{coke})) \times t(\text{max flu})]$. These equations give fairly good fits when $k(\text{melt})$ is in the range 0.5 to 4 min^{-1} and $k(\text{coke})$ is in the range 0.2 to 1.5 min^{-1} . To relate the conceptual molten fraction $[M]$ to the observed ddp, the emf from a model curve is compared with that from the experimental curve. For example, Ohio #9 seam coal at 411° has an experimental emf of 81.3 ddp, and a calculated emf (using the k values of Table 2) of $[M] = 0.683$. When each datum in the model curve is multiplied by the factor 81.3/0.683, the model fluidities are converted to units of ddp. [Detailed procedures and programs for these estimates are available from the authors.]

Effect of Temperature

Isothermal curves were obtained upon Kentucky #11 seam coal at five additional temperatures, in the range 400–460°C. Values of the model constants are given in Table 3. An Arrhenius plot of the model constants $k(\text{melt})$ and $k(\text{coke})$ is shown in Figure 2. For this coal the value of the apparent E_a for $k(\text{melt})$ (best 5 of 6 data) is 173 ± 13 kJ; that for $k(\text{coke})$ (also best 5 of 6) is 228 ± 6 kJ. Viscosities commonly show an analogous "activation energy of viscosity" (18,19). The apparent E_a of maximum fluidity is approximately 600 kJ, high when compared with those for asphalt (120–150 kJ) and glass (390–400 kJ) (20,21).

When the temperature dependencies for the parameters of this model have been estimated from the data of Table 3, isothermal curves may be calculated for any interpolated temperature, or for any extrapolated temperature close to the range of experimental data. Figure 3 shows a family of fluidity envelopes for the Kentucky #11 seam coal, based upon data calculated for the range 392–468°C. Each curve is an "isofluidity" envelope, open at the top. Figure 3 is read along horizontal (isothermal) lines. At 430° this coal exhibits a plastic period (fluidity greater than 1 ddp) from 2 to 30 min., and has a fluidity exceeding 100 ddp from 5 to 20 min. This projection, which will afford markedly different envelopes for different coals, may find use in applications in which the plastic properties of bituminous coals are important.

Discussion

The organic structures of coals are numerous and varied. Bonds which thermally cleave at useful rates at 390–400°C (dissociation energies of 210–230 kJ) are not the same as those cleaved at 460° (240–260 kJ). A major reason for isothermal measurements is to control this variable.

Gieseler fluidity can be related to viscosity units by calibrating with standard fluids. Measurements with the plastometer used in this study and with

appropriate standards (22) in the range 500 - 10,000 poise yield a linear calibration:

$$\ln(\text{poise}) = 16.2789 - 0.96787 \ln(\text{ddpm}) \quad (9)$$

with a correlation coefficient of .9997. Actual coal melts are heterogeneous (7,16), pseudoplastic (23), and viscoelastic in their later coking stages (24). It is nevertheless useful to interpret Gieseler fluidities as estimates of true viscosities.

Nicodemo and Nicolais (25) and Fedors (26) have shown the viscosity of Newtonian suspensions of solids to conform to the expression:

$$\eta/\eta_0 = \exp(a\phi) \quad (10)$$

where η , η_0 , and ϕ are the suspension viscosity, solvent viscosity, and solids fraction. Data obtained by Lee (27) show the logarithm of the maximum fluidity of coal blends to vary linearly with composition. These observations are telling us the same thing: that the logarithm of fluidity, not fluidity itself, is a direct measure of the molten fraction. If we assume that a fluidity of 1 ddpm corresponds to the maximum solid fraction ϕ_{\max} , we can project the relationship:

$$\ln(F) = \ln(F^0) \cdot \left[1 - \frac{\phi}{\phi_{\max}} \right] \quad (11)$$

To use Equation 11 we need estimates of ϕ_{\max} and of the fluidity of pure metaplast, F^0 . The maximum solid fraction in a random dispersion of monodisperse spheres is 0.63 (28,29). This fraction is higher for polydisperse spheres (30) and for some size distributions may be as high as 0.9 (31). For coal melts we will assume a value of ϕ_{\max} of 0.80. If the extrapolated maximum fluidity of the Pittsburgh #8 seam sample at 412° (1.0×10^6 ddpm) is taken as a rough estimate of F^0 , we can estimate solid fractions in other coals from fluidities at this temperature. Fluidities of 10, 100, 1,000 and 10,000 ddpm indicate solid fractions of approximately .67, .53, .40 and .27. The minimum values of ϕ for Ohio #9 and Kentucky #11 samples in Table 2 are approximately 0.55 and 0.41.

The linearity of $\log(F)$ with ϕ has mechanistic implications as well. The left-hand of Equation 3 is more accurately expressed as $d \ln[M]/dt$. The curves of Figure 1 show linear increases of metaplast with time in the early stages, and linear decreases of metaplast with time (zeroth order kinetics) in the later coking stages.

Extrusion pumping of coals in the plastic state entails substantially isothermal operations for residence times of a few minutes in the screw (1-3). Several coals, including those of the present study, have been extruded with no difficulty in JPL's 1.5-in. coal pump. Two coals which showed very little plasticity (less than 2 ddpm) were not extrudable (3). The isothermal plastometry profiles may prove to be a useful tool in predicting behavior in coal pumps. Recent evidence of the substantial effect of pressure upon observed plasticity (10) indicates that this variable should be considered in future work.

Acknowledgments

Christopher England (Jet Propulsion Laboratory) first suggested this study. This work was performed for the coal pump development project, Jet Propulsion Laboratory, California Institute of Technology, under Contract no. 954920. The coal pump project is supported by the Department of Energy through an agreement with the National Aeronautics and Space Administration.

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Table 1

Properties of Three Bituminous Coals

Seam	Ohio #9	Kentucky #11	Pittsburgh #8
source	Noble Co.	Webster Co.	(from METC)
Proximate: ¹			
moisture	2.15%	1.97%	0.79%
ash	18.87	8.34	8.65
vol. matter	39.40	41.19	40.85
fixed carbon	39.58	48.50	49.71
Ultimate: ²			
carbon	79.41	82.21	84.83
hydrogen	5.30	5.43	5.49
nitrogen	1.13	1.36	1.44
sulfur	5.38	3.52	2.92
oxygen ³	8.78	7.48	5.33
Heating value ²	14,010 Btu/lb	14,770 Btu/lb	15,290 Btu/lb
Free swelling index	3	7	7½
Petrographic analysis ¹			
exinoids	2.1%	5.1%	4.0%
vitrinoids	70.1	76.3	75.3
other reactives	1.9	1.2	0.9
inert macerals	12.9	11.0	13.7
ASTM Gieseler plastometry			
softening T	398°C	392°C	372°C
coking T	462°	474°	485°
max flu T	435°	435°	(414-459°)
max fluidity	114 ddpm	6240 ddpm	>>25000 ddpm

¹ As received.² Moisture- and ash-free basis.³ By difference.

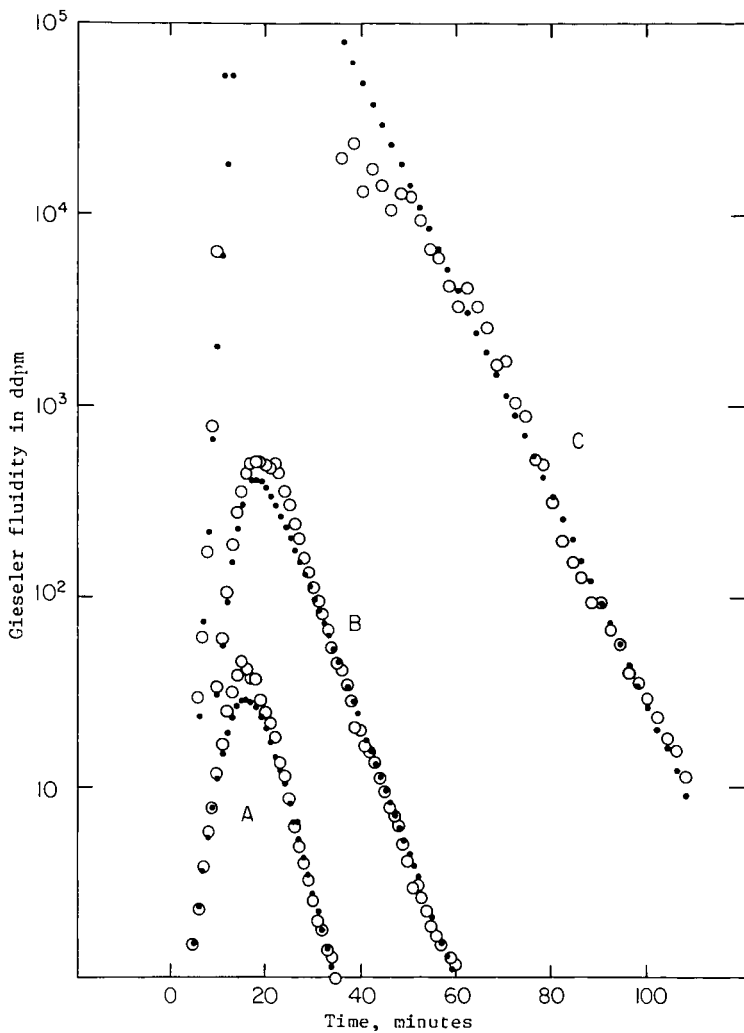


Figure 1. Isothermal plastometric curves of three bituminous coals. A - Ohio #9 seam (Noble Co.) at 411°C. B - Kentucky #11 seam (Webster Co.) at 410°C. C - Pittsburgh #3 seam (from M&TC) at 412°C. Open circles are experimental data; solid points are calculated by the three-parameter model (values given in Table 2).

Table 2

Characteristics of Three Isothermal Plastic Curves at 410-412°C

	Ohio #9 411°C	Kentucky #11 410°C	Pittsburgh #8 412°C
Melting slope	0.425	0.621	1.084
Coking slope	-0.216	-0.151	-0.125
Maximum fluidity, ddpm ¹	81	896	1.0 x 10 ⁶
Time of maximum fluidity ¹	14.3 ₄	15.4 ₂	15.7 ₅
<u>Calculated values:²</u>			
k(init)	6.0 x 10 ⁻⁴	4.3 x 10 ⁻⁵	3.4 x 10 ⁻⁸
k(melt)	0.77	0.79	1.24
k(coke)	0.35	0.16	0.125

¹ By extrapolation of melting and coking slopes.² Using the three-parameter model described in text. Dimensions of k(init) and k(coke) are min⁻¹; k(melt) is min⁻¹ mass fraction⁻¹.

Table 3

Effect of Temperature upon the Isothermal Plastic Curves of Kentucky#11 Seam Coal (400-460°C)

<u>Temperature, °C</u>	<u>400.</u>	<u>410.</u>	<u>425.5</u>	<u>440.</u>	<u>449.9</u>	<u>460.</u>
Melting slope	0.172	0.621	1.35	1.60	2.57	5. ₃
Coking slope	-0.069	-0.151	-0.325	-0.67 ₉	-1.11	-1.5 ₆
Maximum fluidity, ddpm ¹	44	896	2.58E4	3.34E4	8.89E4	2.21E6
Time of maximum fluidity ¹ , min.	25.8 ₂	15.4 ₂	11.1 ₄	8.1 ₂	6.3 ₀	4.1 ₃
<u>Calculated values:²</u>						
k(init)	1.2E-3	4.3E-5	1.9E-6	3.0E-6	6.5E-7	4.3E-7
k(melt)	0.26	0.79	1.74	2.49	4.05	7. ₁
k(coke)	0.083	0.158	0.339	0.84 ₈	1.40	1.6 ₆

¹ By extrapolation of melting and coking slopes.² See Table 2, footnote 2.

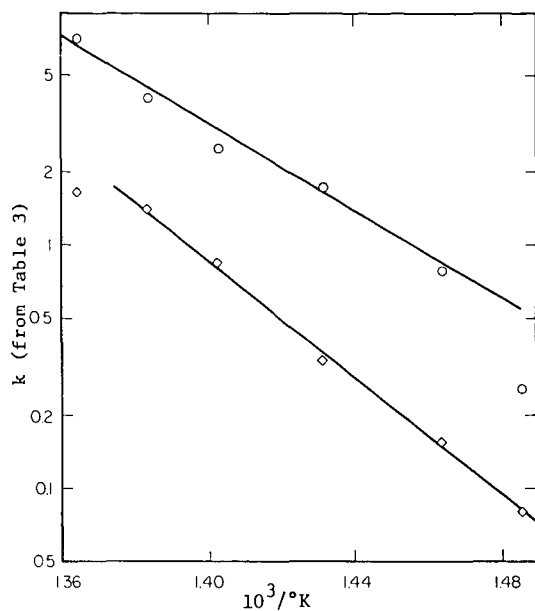


Figure 2. Arrhenius dependency of the model constants $k(\text{melt})$ (circles) and $k(\text{coke})$ (diamonds) for Kentucky #11 seam coal

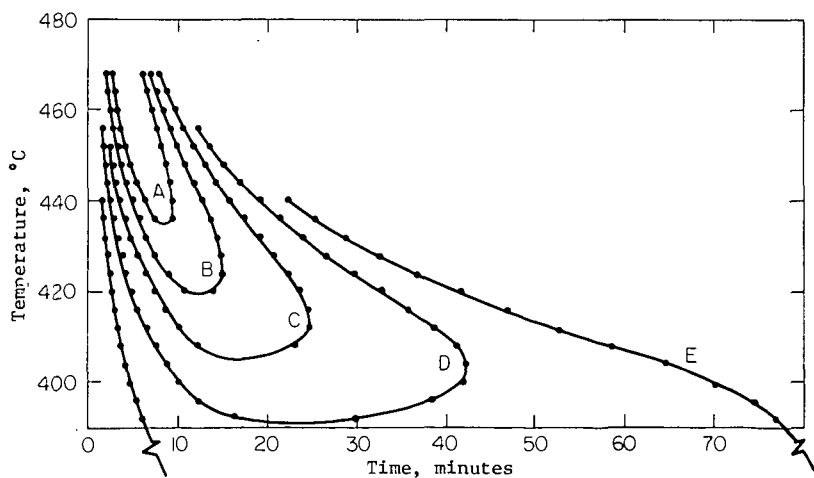


Figure 3. Isothermal fluidity envelopes for Kentucky #11 seam coal
A - 10^4 ddpm. B - 10^3 ddpm. C - 10^2 ddpm. D - 10 ddpm. E - 1 ddpm